SHORT THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PHD)

Application possibilities of reactive polymeric nanoparticles in dentistry

by Melinda Szalóki

Supervisor: Prof. Csaba Hegedűs MD, LDS, PhD

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By **Melinda Szalóki**, chemist

Supervisor: Prof. Csaba Hegedűs MD, LDS, PhD

Doctoral School of Dental Sciences, University of Debrecen

Head of the Examination Committee:
Prof. Ildikó Márton MD, LDS, DSc

Members of the Examination Committee:
Prof. János Szöllősi DSc
Prof. Csaba Dobó-Nagy DMD, PhD

The Examination takes place at 11 a.m., December 12, 2013.

Head of the Defense Committee:
Prof. Ildikó Márton MD, LDS, DSc

Reviewers: Prof. Sándor Kéki DSc
Kinga Turzó PhD

Members of the Defense Committee:
Prof. János Szöllősi MSc, DSc
Prof. Csaba Dobó-Nagy DMD, PhD

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INTRODUCTION

Nowadays the material science research and nanoscience relate to more and more research area. The areas of practical utilizations are expanded with results of these researches. In dentistry meaningful material science research focuses on the area of dental filling materials [1-3]. The dental filling materials have to fulfill many requirements at filling preparation. The dental filling materials are multi component materials. The main components are organic resin matrix, and inorganic filler with surface modified coupling agent. The resin matrix is a mixture of methacrylate/acrylate monomers [4, 5]. During the application the monomers of resin matrix are polymerized to crosslinked polymer structure by free radical non linear polymerization process [5, 6]. Several drawback properties appear at the application as residual monomers can cause allergy reaction, and presence of degradation products [7-11]; polymerization shrinkage [12, 13], so the dimensional stability of filling is lost. The results of these drawback properties are the marginal gap forming between the filling and the structure of the tooth, creating secondary caries [12]. A tensile force is applied to the cavity surface by the volumetric shrinkage. This tensile force can cause tooth materials injury, cusps deflection and fracture. This tensile force is the polymerization shrinkage stress [14].

OBJECTIVES

Our objective is to reduce the drawback properties of dental resin composites by the application of reactive polymeric nanoparticles. Among controlled reaction circumstances polymeric molecules are synthesized with high conversion. The size of particles is tailorable and particles include pendant vinyl groups which can react in post polymerization process.

MATERIALS AND METHODS

Synthesis of reactive polymeric nanoparticles

Early stage of our research started with building of a model system. The nanoparticles were prepared by the emulsion polymerization of styrene (ST; Sigma-Aldrich; USA) and trimethylol propane trimethacrylate

(TMPTMA; Sigma-Aldrich; USA) monomers under inert atmosphere. The polymerization was non linear due to the application of the trifunctional TMPTMA monomer. The surfactant was sodium dodecyl sulphate (SDS, Sigma-Aldrich; USA). The thermoinitiator was potassium peroxide disulphate ($K_2S_2O_8$; Sigma-Aldrich; USA) which formed free radicals at 60 ^{0}C. The concentration of monomers was 5 % (m/m), the initiator was 1 % (n/n), the surfactant was 0.08 mol/dm^3. The ratio of monomers was changed (ST:TMPTMA=1:9; 3:7; 5:5; 7:3 and 9:1) in the formed copolymers. The reaction time was 120 min. At the end of polymerization latex particles were formed, which were precipitated by methyl alcohol in order to unseal the emulsion. The dispersion was centrifuged (Heraeus, Biofuge 22 R; Germany) at 5 ^{0}C, 114000 rpm for 20 min. The polymer was dried till constant weight in vacuum at room temperature.

After studying the model system the styrene monomer was replaced to methyl methacrylate (MMA; Sigma-Aldrich; USA), which is often used monomer in dentistry. The MMA-TMPTMA copolymer was synthesized by the same method as the ST-TMPTMA copolymer. Two different crosslinked nanoparticles were chosen (MMA:TMPTMA=7:3; MMA:TMPTMA=3:7) to form nanocomposites.

Experimental dental resin and their composites

The experimental dental resin consisted of bisphenol A glycol dimethacrylate (Bis-GMA; Sigma-Aldrich; USA), triethylene glycol dimethacrylate (TEGDMA; Sigma-Aldrich; USA) in 50:50 % (m/m) with 5 % (m/m) etoxylated bisphenol A glycol dimethacrylate (Bis-EMA; Sigma-Aldrich; USA). The photoinitiator was camphorquinone in 0.2 % (m/m) (CQ; Sigma-Aldrich; USA). In this monomer mixture 5, 10, 15, 20 and 25 % (m/m) nanoparticles (MMA:TMPTMA= 3:7 and 7:3) were stirred by ultrasound bath.

Characterization of reactive polymeric nanoparticles

Nuclear magnetic resonance spectroscopy (^{1}H NMR)

The structure of copolymer and detection of reactive functional groups were carried out ^{1}H NMR (Bruker 200 WP; USA) at 200MHz operating frequency in deuterated chloroform solution ($CDCl_3$; Sigma-Aldrich; USA). The reference was tetramethyl silane (TMS). The ratios of monomers in copolymer structure were calculated by integrals of NMR signs and Kelen-Tüdős method. The number average vinyl functionality (NAVF) was introduced to express the quantification of pendant vinyl groups. The polymer samples were exempted from residual monomer for the calculations of monomer ratios in copolymer and NAVF. For this process polymer samples were dissolved or dipergated in toluene and precipitated in methyl alcohol. For this calculation the samples were dissolved highly deuterated chloroform solution (99.96 atom% $CDCl_3$) at the concentration of 18.75 mg/ml.

Transmission and scanning electron microcopy (TEM, SEM)

The toluene polymer dispersions were placed on carbon coated TEM copper grid. The solvent was evaporated at room temperature after the samples were covered in vacuum by thin gold layer (8-10 nm) to avoid the static charge of polymer samples. The TEM photos were taken by a JEOL2000 FX-II; Japan. In this case the size of nanoparticles and size distribution were determined in dried form.

The distribution of nanoparticles in cured modified dental resin was analyzed by scanning electron microscopy (SEM; Hitachi 3000N; Japan). The photos were taken from the gold covered surface fracture of the polymerized specimen.

Dynamic Laser Light Scattering spectroscopy (DLS)

The size of latex samples were analyzed in distilled water. The hydrodynamic diameters of prepared nanoparticles were measured in toluene by DLS photometer (BI-200SM Brookhaven Research Laser

Light Scattering; USA) equipped with a NdYAg solid-state laser at an operating wavelength of 532 nm. The samples were thermostated at 25^0C and the measuring was performed at 90^0 angle detection. Each sample was measured three times.

Transparency studies

Transmittance of polymer dispersion was measured in toluene by spectrophotometer (Unicam SP 1800 UV; UK) at an operating wavelength 480 nm in optically homogenous quartz cuvettes.

Characterization of modified dental resin

Polymerization shrinkage measurements

The polymerization shrinkage of unfilled and dental composites was determined with a commercial density determination kit of an analytical balance (Adam Equipment PW 254; UK) by the Archimedes principle. The tests were in distilled water at controlled temperature (20 ± 4^0C). The samples were placed into a small glass container and the densities of samples were measured before and after polymerization. According to the mass conversation law the volume changes were calculated during the polymerization. The photopolymerization was in a photopolymerization chamber (Dentacolor XS, Heraeus Kulzer; Germany) at λ_{max}=435 nm for 90 sec. The reference was the unfilled dental resin. For each measurement fifteen specimens (n=15) were prepared. During the measurements the density changing of water at different temperatures was taken into account.

Rheology measurements

The viscosity values of dental resin and nanocomposites were measured by a rotation rheometer (AR 550, TA Instruments; USA) equipped with cone-plate accessory. This consisted of a rotating cone and a stationary plate. The sample was filled (8 ml) in the gap between them (60 µm). Cone angle was 1^0 59’ 38” and diameter was 60 mm, 2^0 standard steel cone. The device contains an air bearing, which required the provision of a minimum of 2.5 bars pressure. The apparatus is equipped with a temperature unit (Peltier plate) that gives a good temperature control (20 ± 5^0C) over an extended time.

Each sample was measured three times and the data were evaluated by Rheology Advantage Data Analysis software (TA Instruments Ltd., version 4.1.2.).

Flexural strength measurements

The three point flexural strength tests were implemented on prismatic specimens with a mechanical testing device (ISTRON 5544; USA). The parameters of specimens were 2 mm x 2 mm and its length was 20 mm. The samples were photopolymerized in Teflon mold for 90 sec (Dentacolor XS, Heraeus Kulzer; Germany, λ_{max}=435 nm). Fourteen specimens were made from each sample and that were stored at room temperature for 24 hour before testing. The distance of spams was 18 mm. The crosshead speed was 1 mm/sec. The flexural stress (FS) and flexural modulus (FM) were calculated by MSZ EN ISO 178.

Polymerization shrinkage stress measurements

During the photopolymerization process a tensile force affects to the cavity wall. This tensile stress, as polymerization shrinkage stress, was measured with a mechanical testing device (INSTRON 5544; USA). Two glass rods (8 mm in diameter x 25 mm in height) were placed opposite each other in a vertical position in the testing machine. Before every measurement the surface of glass rods were gently sandblasted with 50 µm sized Al_2O_3 (clinical-sandblaster; Henry Schein Inc.; USA). The remaining aluminum oxide was removed by compressed air and after that the glass surface was rinsed with acetone. The sandblasting process ensured an increased surface roughness and removed residual cured sample from the glass rods. The samples were photopolymerized with dental halogen light-curing unite (Translux EC; Heraeus Kulzer GmbH; Germany) at 435 nm wavelengths for 200 sec. For each measurement fourteen specimens were prepared. The distance between upper and lower rods was standardized in 0.8 mm. This gap was filled with sample resin. The C factor expressed the ratio of bounden surface to unbounded surface. This configuration resulted in C-value of 5 (C=r/h; where r is the radius of disk, h is the height of sample, i.e. 0.8 mm).

Compressive strength measurements

Compressive strength of reference and reinforced resins were investigated with a mechanical analyzer (INSTRON 4302; USA). The compressive tests were performed on cylindrical specimens with the full scale load range of 10 kN and 1 mm/sec crosshead speed. The cylindrical samples had a diameter of 5 mm and specimen length of 5 mm. The samples were polymerized in Teflon mold for 90 sec (Dentacolor XS polymerization chamber unit, Heraeus Kulzer; Germany, λ_{max}=435 nm). Fourteen specimens were prepared and stored for 24 hours at room temperature. The compressive stress (CS) data were calculated MSZ EN ISO 604.

Diametral tensile strength measurements

The diametral tensile strength (DTS) of reference and reinforced dental resin were measured with mechanical testing device (INSTRON 5544; USA) equipped with 2 kN load cell at cross head speed of 1mm/sec. The specimens were 3 mm in height and 6 mm in diameter. The uncured resins were placed into a Teflon mold and the samples were coved by a thin film and cured for 90 sec in a chamber unit (Dentacolor XS, Heraeus Kulzer; Germany, λ_{max}=435 nm). Before testing the samples were stored for 24 hours at room temperature. Number of specimens was between 18 and 24. The specimens were placed in diametral position into the mechanical testing device and the maximum compression load (F) at fracture has been diagnosed. The DTS was calculated as $DTS=2F/(\pi hd)$ where F is the compression load, h and d the parameters of specimens and π constant is 3.14.

Statistical analysis

The (non-parametric) Mann-Whitney (MW) test was applied to compare the different groups of data. This test is also referred as a natural non-parametric alternative of the Student-t test for the comparison of means. In our case, it is suggested to prefer MW test to t-test due to the relatively small sample sizes and the possible lack of normality of the distributions. Note that one can calculate both the exact significance and asymptotic significance for this test. Since in all cases the same result was concluded, based on both, but only the later one is shown in the tables. The statistical analyses were performed by using SPSS version 17.0 software.

RESULTS AND DISCUSSION

Characterization of ST-TMPTMA reactive polymeric nanoparticles

The conversion values of the model copolymer were high. The NMR spectra of polymer samples proved the presence of pendant vinyl groups in nanoparticles between 5.2 and 6.4 ppm. The intensity of vinyl peaks is related to the trifunctional monomers content and reaction time. At high concentration of TMPTMA and in the early stage of polymerization the intensity of vinyl peaks is high. However at prolonged reaction times, as 4 and 8 hours, the vinyl signals decline to very low or near zero intensity due to the inter- and intramolecular reactions. Based on the Kelen-Tüdős equation the relative reactivity ratios for styrene was r1=1.44 and for TMPTMA monomer was r2=1.41, respectively. The value of two reactivity ratios was similar to each other, thus ideal copolymerization was in ST/TMPTMA copolymer. The monomers built into the copolymer chain in random way and the composition of monomer and copolymer were equal.

According to the DLS measurements the size and the size distribution of latex particles of ST-TMPTMA copolymer increased with the trifunctional monomer concentration. The smallest size was 25.4 nm at ST:TMPTMA=9:1 composition and the highest one was 497 nm with wide distribution at ST:TMPTMA=1:9. This can be explained by the hydrophobic and hydrophilic nature of the monomers. The styrene monomer is highly hydrophobic, but TMPTMA is miscible with water due to the ester linkage. This fact was justified with an experiment. The mixture of monomers with increasing TMPTMA monomers were sonicated with water without surfactant. The organic layer became opaque as the ratio of trifunctional monomer increased. Result of slight hydrophilic nature of the TMPTMA monomer was that water in oil-in-water (w/o/w) emulsion has been formed when the TMPTMA ratio increased.

The DLS measurements of toluene dispersion of polymeric nanoparticles showed that the size of nanoparticles increased with the mole ratio of crosslinker monomer till ST:TMPTMA=5:5 composition. At higher TMPTMA concentration the size of nanoparticles decreased due to the crosslinking process. The covalent chemical bounds (crosslinking bounds) were not allowed to swell the nanoparticles in toluene. We could establish that the size distribution of nanoparticles was wider in toluene than latex particles in distilled water. This fact justified that more individual polymeric nanoparticles were formed inside the micelles. The size of nanoparticles depended on the concentration of TMPTMA, which determined the crosslinking density and swelling behavior of polymeric nanoparticles.

The transmittance studies showed that the highest transmittance was observed at ST:TMPTMA=9:1 and ST:TMPTMA=1:9 compositions. The less crosslinked polymer, namely ST:TMPTMA=9:1, behaved as a linear polymer, thus the polymer was able to stretch out. At high crosslinking density the nanoparticles were not able to swell thus more light passed through the dispersion. The lowest transmittance was at ST:TMPTMA=7:3 copolymer due to the bigger polymer particle size and higher swelling capacity.

Characterization of MMA-TMPTMA reactive polymeric nanoparticles

The monomer ratio of MMA:TMPTMA copolymer was 3:7 and 7:3. The yield was high at both macromolecules. The conclusion from the model system was correlated in MMA/TMPTMA system too. The highly crosslinked nanoparticles showed low particles size, namely at 3:7 was 208±28.92 nm, at 7:3 was 595±89.9 nm, respectively. The NMR spectra verified the presence of pendant functional groups in nanoparticles. Based on TEM pictures the size of particle is in accordance with the result of DLS measurements. The size distributions of MMA:TMPTMA=3:7 was wider than 7:3 copolymer.

Characteriazion of MMA-TMPTMA reactive polymeric nanoparticles modified dental resin

The modified dental resin was formed by the mixing of experimental dental resin and increased gradually MMA/TMPTMA copolymer from 5 % (m/m) to 25 % (m/m). The reactive pendant double bounds of nanoparticles and the unsaturated carbon double bounds of monomers reacted with each other in order to influence such mechanical properties of dental composites as polymerization shrinkage, polymerization shrinkage stress, diametral tensile- flexural- and compression strengths.

The rheology analysis of nanocomposites showed that the viscosity values exponentially increased with nanoparticles content. This was explained by the swelling of nanoparticles in dental resin. The less crosslinked nanoparticles were able to swell in higher rate what was resulted in the viscosity elevating. According to the shape of viscosity-shear rate curves it can be established that the reinforced dental resin behaved as a Newtonian fluid. However hysteresis loops were observed at high amount of nanoparticles (25 % (m/m)) indicating the structural viscosity.

The polymerization shrinkage analysis showed that PS value decreased with increasing of nanoparticles content. Based on the statistical analysis this reduction was significant compared to reference, unfilled dental resin.

The polymerization shrinkage stress values decreased by the presence of MMA/TMPTMA nanoparticles. The significance values increased with the nanoparticles content. The less crosslinked nanoparticles reduced the shrinkage stress in higher degree due to higher swelling ability. The less crosslinked nanoparticles were more permeable for dental monomers. Like in all nanosystem we had to reckon with the aggregation which was consequence of the high surface energy of the particles resulting from the small size. Small clusters were formed by the aggregation of nanoparticles, which were not wet completely by the monomers of dental resin as well. This incomplete penetration resulted voids not only in the cluster, but inside a nanoparticles. Surface energy of empty voids decreased, which is energetically favourable. During the polymerization this voids had shrunk what meant an increased volume for the cured dental resin. This is the reason that the voids are able to decrease the polymerization shrinkage stress. The polymerization of trapped resin in the clusters reduced the surface, thus polymerization shrinkage stress, too.

We investigate the efficacy of reactive polymeric nanoparticles to flexural strength of nanocomposites. The statistical analysis showed that the modified dental resin differed significantly from the unfilled resin. The FS values increased with nanoparticles content up to 15 % (m/m). At higher amount of nanoparticles this tendency was deteriorating due to the cluster forming ability of nanoparticles.

The compressive strength method helps to investigate the efficacy of nanoparticles in bulk and its effect on the compressive stress of cured nanocomposites. The measurements showed that the compressive strength data of nanocomposites increased with nanoparticles. Above 15 % (m/m) the CS values of nanocomposites decreased due to the inhomogen distribution and aggregation of nanoparticles. The empty voids, which were formed among the aggregated nanoparticles, generated an internal stress during the compression load.

The diametral tensile strength measures the cohesive strength of a material. The cohesive properties of the material depend on the load necessary to fracture and independt from the deformation. As expected the highest DTS value was at unfilled reference resin due to homogeneous structure. The inhomogenity of materials was increased by the mixing of nanoparticles into the dental resin resulting in lower DTS values. The less crosslinked nanoparticles modified dental resin showed higher DTS values in accordance with other methods.

SUMMARY

In our research work synthesis of reactive polymeic nanoparticles (RPNPs) and their effect on mechanical properties of dental resin were introduced.

Polymeric nanoparticles were prepared with high yield by emulsion polymerization process. According to our future plan the structural analysis of copolymer justified the presence of pendant functional groups in nanoparticles. The reactivity, size and size distribution of nanoparticles was tailorable by the amount of trifunctional monomers. The dental polymeric nanocomposites were formed by the mixing of RPNPs and dental resin matrix. According to the testing methods it can be established that the prepared nanoparticles had a significant effect on mechanical properties of nanocomposites. The polymerization shrinkage and stress are drawback properties of a dental filling material, which can be reduced by the presence of nanoparticles. The flexural and compressive strengths increased at the comparison of reference and nanocomposites. The toughness of dental resin was increased by the application of PRNPs. However the advantage of crosslinked structure of RPNPs, in above mentioned parameters, caused increased viscosity values. Thus the application possibility of inorganic filler to these nanocomposites is limited. The composites, as inhomogeneous materials, decreased the cohesive energy which was reflected on the deteriorating diametral tensile strength value.

NEW SCIENTIFIC ACHIEVEMENTS

- Reactive polymeric nanoparticles were formed by the emulsion polymerization of mono- (styrene, methyl methacrylate) and trifunctional (trimethylol propane trimethacrylate) monomers. The reactivity of nanoparticles was derived by pendant vinyl groups.
- I determined that mole ratio of TMPTMA influenced the reactivity, crosslinking density, size and size distributions of prepared nanoparticles. Thus the size and reactivity of nanoparticles were tailorable among certain reaction conditions.
- I justified that the RPNPs could be used to reduce the drawback properties of dental resin.
- I demonstrated that MMA-TMPTMA copolymer nanoparticles had effect on such mechanical properties of dental resin, as viscosity, polymerization shrinkage, polymerization shrinkage stress, diametral tensile-, flexural- and compressive strengths.

New developments of polymeric dental filling materials are mainly focused on the reduction of polymerization shrinkage stress, improvement of biocompatibility, wear resistance, durability. This can be partially achieved by synthesizing of new dental monomers and their composites, using special structure filler (core-shell) [15] and optimizing of inorganic filler and photopolymerization process [1, 16, 17].

Reactive polymeric nanoparticles, which are presented in our work, may be suitable for the development of dental filling materials. However, further optimization is required for the applicable of this type of particles and systems.

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List of publications related to the dissertation

1. **Szalóki, M.**, Gáll, J., Bukovinszki, K., Borbély, J., Hegedűs, C.: Synthesis and characterization of cross-linked polymeric nanoparticles and their composites for reinforcement of photocurable dental resin.
   React. Func. Polym. 73 (3), 465-473, 2013.
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3. Üveges, A., **Szalóki, M.**, Hartmann, J.F., Hegedűs, C., Borbély, J.: Synthesis of Polymeric Nanoparticles by Cross-Linking Copolymerization.
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List of other publications

Szalóki M., Bukovinszki K., Üveges A., Hegedűs C., Borbély J.: Fogászati kompozitok gyantájának módosítása reaktív polimer nanorészecskékkel.
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2. Magdolna Bodnar, **Melinda Szaloki**, Adrienn Veres, Imre Borok, Janos Borbely: Synthesis of polymeric nanoparticles; 2nd European Student Conference on Physical, Organic and Polymer Chemistry, Vienna, Austria (2004)

3. Janos Borbely, **Melinda Szaloki**, John F. Hartmann, Csaba Hegedus: Preparation of reactive polymeric nanoparticles; The 231st ACS National Meeting, Atlanta, GA, USA (2006)

4. **Melinda Szaloki**, Zsolt Dudas, John F. Hartmann, Janos Borbely: Preparation of Reactive Polymeric Nanoparticles (RPNPs) in emulsion; 9th Conference on Colloid Chemistry, Siófok, Hungary (2007)

5. **Szalóki Melinda**, Borbély János: Polimer kompozitok előállítása fogászati alkalmazásra; VIII. Téli iskola, Balatonfüred, Magyarország (2008)

6. Katalin Bukovinszki, **Melinda Szalóki**, Andrea Uveges, Zsolt Dudas, John F. Hartmann, Csaba Hegedus, Janos Borbely: Nano-sized organofillers for restorative dentistry; 235th ACS National Meeting, New Orleans, USA (2008)

7. **Melinda Szaloki**, Janos Borbely, Csaba Hegedus: Influence of polymeric nanoparticles to resin matrix of dental composites; 88th Generel Session & Exhibition of the IADR, Barcelona, Spain (2010)

Posters connected to this thesis:

8. **Szalóki Melinda**, Skribanek Róbert, Dr. Borbély János: Oldószermentes polimer filmek előállítása; IX. Szemcseméret-analitikai, Környezetvédelmi és Portechnológiai Nemzetközi Szimpózium, Balatonfüred, Magyarország (2004)

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21. Géza Vitályos, **Melinda Szalóki**, Jolán Hársfalvi, Csaba Hegedus: Binding of oligopeptide to polymethyl methacrylate surface; IADR General Session, Iguacu Falls, Brazil, (2012); lecture

22. Julia A. Burunkova, K.B. Mazanov, V.G. Bulgakova, I.Yu. Denisyuk, **M. Szaloki**, S. Kokenyesi: TiO2-Acrylate Nanocomposite Elaborated by UV-Curing with Tanable Properties; Proceedings of the International Conference on Oxide Materials for Electronic Engineering (OMEE-2012) Lviv, Ukraine (2012); poster

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